Study of Structural, Optical, and Photocatalytic Exploration of Nickel Oxide Nanoparticles by the Incorporation of Trivalent Metal Ions

SYNOPSIS

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Shilpa Thakur
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Under the supervision of

Dr. Rajender Kumar
(Associate Professor)

DEPARTMENT OF PHYSICS
SCHOOL OF BASIC & APPLIED SCIENCES
CAREER POINT UNIVERSITY HAMIRPUR
TIKKER (KHARWARIAN), BHORANJ
HAMIRPUR (HP)-176041, INDIA

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1. Introduction

1.1 Nanotechnology

Nanotechnology (NT) is a merging of different fields of science that allows for the creation of various devices in the medical, agricultural, and electronic fields (Sivakami, Sarankumar, and Vinodha, 2021). By the rapid growth of NT some of the fields such as nanobiotechnology, quantum dots and applied microbiology are new technologies that have appeared (Dubey et al., 2022). The word "nano" arrive from the Greek word "nano," which indicates "dwarf". For the metric scale, this nanowords implies one billionth of a meters or 10^{-9} meters. It is the most appropriate length unit for representing the size of a single molecule. Nanoscopic objects are too tiny and not seen with the naked eye (Gaines, 2015). Nanoscience and NT overlap with biological sciences with numerous points. Metabolites, motors, membranes, nucleic acids of biological systems are also all made up of a collection nanodevices (Rajwar et al., 2020). The physical and chemical properties of the substance changes, as when the thickness of a material is reduced from macroscopic to nanometers (Singh and Singh, 2017).

NT is a subcategory of science and engineering devoted with materials for measurements of one hundredth of a nanometer or less (Milojevic, 2012). NT includes by controlling the dimensions and size of nanoparticles (NPs), we can adjust their optical, electronic, and electrical features. Of course, perfectly randomly oriented metal nanoparticles (NPs) are ideal, but exceptional behaviors should then be sought even if the ideality isn't obtained perfectly. Metallic NPs offer a variety of forms, such as gold, silver, compounds, magnetic NPs, so on and so forth.

The word "nanotechnology" refers to the formation and application of very small dimensional particles. Metal NPs has various properties and qualities which differentiate them from bulk materials. Due to the size and morphology, metal NPs gave numbers of exceptional opportunities used for technological advancements. (Heiligtag & Neiderberger, 2013) Metallic NPs also have been used in medical applications (targeted drug delivery, antifungal and antibacterial action)(Matatkova et al., 2022). By achieving the knowledge of NT, Researchers formulate the size of materials according to their desires. It is wide field with experimental and theoretical science for the workers (Dange et al., 2017).

1.2 Nanoparticles (NPs) and their Properties

NPs have a distinguished and long history. NPs are clusters of atoms, ions or molecules (Johnston, 2012). When we compare the size of the marble with the earth, it just like a nanoscale. NT has been studied since over a century. Since Nobel prize winner Richard P. Feynman used the term in his well-known 1959 lecture "There's Plenty of Room at the Bottom," there have been numerous different advances in the field of NT. A number of different of nanomaterials have emerged as a consequence of nanotechnology. NPs are a broad class of materials composed of particulate substances with a required dimension of 100 nm. (Khan, Saeed, and Khan, 2019). Depending on the size, the materials can be classified as 0D, 1D, 2D, or 3D. (Tiwari, Tiwari & Kim, 2012). NPs are the main and one of the most utilized areas of study in modern material sciences (Padalia, Moteriya & Chanda, 2015).

As earlier discussed, NPs are unique and good possibilities for a variety of applications related to their thermodynamic aspects such as huge surface area, superior mechanical, light absorption, and chemical reactivity. In the following part, we'll go through some of their most crucial characteristics. The optical and electrical properties of NPs are much more intertwined. Noble metal NPs, for illustration, have size-dependent optical characteristics and a significant UV-visible suppression band that is distinct again from bulk metal's band.

1.3 NiO Nanoparticles

The inorganic compound nickel oxide, seems to have the formula Nickel oxide (NiO). NiO is a popular cubic lattice nanostructure that is employed in a variety of applications. NPs find applications in a diverse range of fields such as battery electrodes, electronic devices, ion storage materials, gas sensors, superconductors, thermoelectric metals, catalysts, fuel cells, organic photocathodes, electrochromic films, and in medical applications such as anticancer treatments, cytotoxicity studies, and glucose monitoring devices. NiO is a useful semiconductor with a wide range of applications including photocatalytic degradation, electrodes, photochromic lights, and sensing. NiO is also important to the formation of nickel cermet for use in the anode layer of solid oxide fuel cells, in lithium NiO cathodes for lithium ion electronic service, in electrochromic coatings, plastics, and textiles, as well as in nanowires, nanofibers, and precise alloy and catalyst software products. Sometimes used in airline light weight

structural components, active optical filters, rechargeable battery cathode materials, and substances for gas or temperature sensors which including CO, H, and formaldehyde devices as a promoter and diamagnetic layers. NiO adopts the NaCl structure, with octahedral Ni^{2+} and O^{2-} sites. The conceptually simple structure is commonly known as the rock salt structure. Like many other binary metal oxides, NiO is often non-stoichiometric, meaning that the Ni:O. The lattice parameter of NiO NPs is 2.08 A^{o}.

1.4 Doping

Doping is the process of adding impurities to the intrinsic semiconductors to alter their properties. When an intrinsic semiconductor is doped with Trivalent impurity it becomes a p-type semiconductor. There are enhancement of various properties of the electronic structure of a semiconductor by the addition or doping with metal cations, non-metal anions (Marschall & Wang, 2014). Doping of different dopants has resulted in changing the mixed valance states, differing the surface oxygen vacancies, and adjusted chemical affinity towards various properties (Dey, 2018). When transition metals are doped into the semiconductor, they introduce impurity levels between the conduction and valence bands. These levels act as intermediary states that facilitate the relaxation of excited electrons following photon absorption. These impurity states can be categorized as acceptor levels, deep recombination centers, or shallow donors. They play a crucial role in providing recombination centers for excitons, which are composed of electrons (e^{-}) and holes (h^{+})(Pelaez et al., 2012). Doping may also impact the grain size and surface area of NiO NPs, which in turn affects their catalytic and optical properties. Doping can modify the bandgap of NiO, potentially reducing it and shifting its optical absorption spectrum (Aswathy et al., 2022). This can expand its absorption range into visible light, making it more suitable for photocatalytic applications.

2. Literature Review

There is various works done on the NiO NPs in various fields which can be discussed below:

Cuomo et al. (2016) successfully prepared nanocrystalline NiO, chromium, and cobalt doped NiO NPs using the chemical precipitation method. NiO, Cr, and Co-doped NiO NPs have grain sizes of 10.33 nm, 9.54 nm, and 8.70 nm, respectively. At 314.96 nm, 308.64 nm, and 305.37 nm, the UV absorbance

investigation reveals a pronounced absorption edge. NiO, Cr, and Co-doped NiO NPs had band gaps of 3.93 eV, 4.01 eV, and 4.06 eV, respectively. The addition of chromium and cobalt to NiO NPs changed the magnetic behaviour dramatically, converting the material from superparamagnetic to ferromagnetic.

Lalithambika et al. (2016) synthesized the ZnO and NiO NPs using green method. It was noted that the synthesized ZnO and NiO NPs have high crystalline quality with an average crystallite size of 35 and 30 nm respectively. Degradation percentage of methylene blue was 79.5 % and 88.8 % for NiO and ZnO NPs. The antibacterial properties for both NiO and ZnO NPs were good for E.coli and S.aureus. Nasseri, Ahrari and Zakerinasab (2016) obtained NiO NPs were employed as a green and recyclable nanocatalyst for the manufacture of quinoline derivatives, according to one-pot reaction of 2-aminobenzophenone and different carbonyl compounds generates the products in good to high yield (60–90%).

Kaviyarasu et al. (2016) synthesized and characterized of NiO nano rods generated by the sol-gel method. The NiO nanorods have a pure cubic phase crystallinity structure, as seen by the XRD pattern. No rods with diameters up to 5nm were produced, according to XRD and HRTEM. The broad band in NiO doped to raise temperatures has caused an increase in the absorption spectra, which has gradually increased peaks.
Gnanasekaran et al. (2017) obtained metal oxide (CeO_2, CuO, NiO, Mn_3O_4, SnO_2 and ZnO) by coprecipitation method. XRD study analysed that the crystallite size of the prepared NPs were in nano size. The morphology and dimension of the synthesized metal oxides were identified through FE-SEM and TEM techniques. Additionally, the synthesized single digit metal oxides NPs were magnificently applied for the degradation of methyl orange and methylene blue under UV light irradiation. It was concluded that the ZnO NPs showed highest photocatalytic degradation of both methyl orange and methylene blue dyes.

Layek and Verma (2016) reported that Mn-doped NiO NPs of the series $Ni_{1-x}Mn_xO$ (x= 0.00, 0.02, 0.04 and 0.06) were successfully produced using a low temperature hydrothermal technique. Temperature dependent magnetization investigation utilising vibrating sample magnetometer (VSM) in high vacuum reveals that the ferro-magnetic Curie temperature for the identical material is 653 K. Balamurugan, Linda Philip and Vidya (2016) in this paper synthesized of NiO NPs. Workers used urea as a fuel and nickel nitrate as an oxidant in a simple solution combustion. HRSEM pictures reveal the aggregation of small particles with particle sizes ranging from 19.5 to 22.4 nm.

The antiferromagnetic property of NiO NPs as synthesised is shown by their room-temperature magnetism.

Soofivand and Niasari (2017) prepared $Ni(acac)_2$ nanostructured by using sublimation method. After uniform $Ni(acac)_2$ nanostructures were considered as an appropriate precursor for synthesis of NiO NPs by thermal decomposition method. Finally, NiO/ graphene nanocomposite (NiO/G) was successfully synthesized by the pre-graphenization route. Various characterization such as SEM, TEM, EDS, VSM, and XRD have been used to determined the shape, element present, magnetic behaviour and phase of the formed materials. Increasing the surface and decreasing the possibility of (e^- h^+) recombination of nanocomposite were led to the better photocatalytic performance of NiO/graphene nanocomposite than pure NiO. According to the obtained results, degradation of methyl orange (MO) in the presence of NiO/graphene nanocomposite under UV and visible light as about 90.3 % after 75 min, and 78 % after 180 min, respectively.

Senobari and Kaewmuang et al. (2018) synthesized the nanosized NiO NPs using solvothermal calcination process. They investigated the effect of varying the calcination temperature from 500 to 700 °C on crystallinity and particle size of the synthesized NiO NPs. It was found that the NiO with smaller particle size and larger surface area shows strong UV–Vis absorption. The NiO NPs calcined at 500°C degraded Congo red under the xenon light better than those calcined at higher temperatures.

Senobari and Nezamzadeh (2018) studied the Effects of coupling, calcination temperature and mole ratio of NiO and CdS NPs were studied on the enhancement of their photocatalytic activities towards methylene blue (MB). Among the NiO NPs calcined at different temperatures, the best activity was obtained for the prepared one at 200 ^oC. In changing the mole ratio of the semiconductors in the coupled systems, the best activity was obtained for mole ratio of 1:4 NiO/CdS. The quadratic model was well fitted to the experimental data (with values of 0.9920 and 0.9833 for R^2 and R^2_{adj}). The best degradation removal of MB was obtained at pH 3.5, catalyst dosage of 0.9 g L^{-1}, 3.2 mg L^{-1} of MB at irradiation time of 83 min.

Bhat et al. (2019) synthesized NiO of size with 30 nm using coprecipitation method. The morphology, particle size, surface area and pore size of NiO NPs were determined by TEM, XRD and BET. FTIR and UV–Visible analysis confirmed the formation of NiO NPs. The photocatalytic degradation of CR dye was analyzed by four parameters such as the concentration of CR dye, the effect of contact time, the effect of

pH and dose of NiO NP catalyst. The maximum degradation of CR dye (84%) by NiO NPs was determined with respect to contact time. The bacterial strains such as *K. pneumonia* 700603 and *B. subtilis* 5902 showed maximum zone of inhibition (15 mm) at 40 mg/ml concentration, and minimum inhibitory concentration 62.5 μg/ml by NiO NPs, respectively.

Sabouri et al. (2019) synthesized NiO NPs by using sol-gel method. Chitosan has been appointed to perform polymerization and function as an endpoint agent throughout this project to grow the particles, as well as carrying out the procedures of preventing agglutination, increasing stability, and reducing toxicity, respectively. the photocatalytic effects of NiO NPs on methylene blue (MB) degradation have been investigated and in accordance with the obtained results, they contain great potential as photocatalysts under UV light. To further analyze the safety of NiO-NPs, the evaluation of their biocompatibility on human cancer U87MG cell lines has been performed by the means of MTT assay, which has indicated cell toxicity at concentrations up to 8 mg/mL.

Bashir et al. (2019) degraded the free cyanide solutions under Ultra voilet light by using biosynthesized NiO NPs. They utilized the Persea americana seeds for green synthesis of nanocatalysts. NiO NPs were determined by XRD, TEM, EDS, UV–Vis analysis, and FTIR spectroscopy. The XRD results indicated a cubic-type structure with space group *Fm*3*m*, No. (225). Morphological analysis conducted using TEM showed that the NiO NPs had rhombohedral and spherical shapes with slight agglomeration. The particle size calculated based on the TEM results was 11 nm. EDS analysis confirmed the elemental constituents of the samples with Ni and O atoms.The NiO NPs performed well as a photocatalyst under UV light during the photodegradation of FCN, where the maximum photocatalytic oxidation efficiency was 84 % after irradiation for 30 min.

Roopan et al. (2019) have prepared NiO NPs using Calotropis gigantea latex (CGL) through green synthesis method in which the latex acts as a capping agent. Further the synthesized NiO NPs were subjected to various analytical techniques like UV–Visible spectroscopy, TEM, XRD, EDX, Particle Size Histogram and Zeta potential. the synthesized NiO NPs were subjected to degrade toxic diazo dye Congo red (CR) and organic compound 4-Nitro phenol in the presence of sunlight within short duration of time. The results indicate that the NiO NPs degrades 95 % of CR and 94 % of nitro phenol.

Vidya and Balamurgan (2019) investigated the photocatalytic degradation of methylene blue dye using PANI (polyaniline) and PANI-NiO (polyaniline-NiO)

nanocomposite as a catalyst. The PANi - NiO nanocomposite has high surface area 23m^2 /g and it degrades 76 % of dye molecules under visible light irradiation. These results indicate that the PANi – NiO nanocatalyst could be employed as an efficient photocatalyst to remove MB dye. Further, the easy synthetic method may be used for the synthesis of diverse NiO doped conducting polymers which might focus on the existing concern of environmental pollution.

Imran din et al. (2019) synthesized Ni and NiO NPs by green approach using seeds extract of Hordeum vulgare plant. The seeds extract of Hordeum vulgare plant which is rich in phenolic content and antioxidants was utilized for reducing the precursor metal salt into NPs. FTIR spectrum revealed that amines and phenolic groups of the plant were responsible for the formation and stabilization of Ni NPs. The degradation of MB dye followed 1st order kinetics.

Amita et al. (2019) synthesized the pure and Cu-doped NiO NPs by using coprecipitation method. To determine the physical properties of said NPs, these NPs were characterized by using XRD, FTIR, and UV-Vis spectroscopy. The photo-reduction activities of prepared samples were evaluated using a cationic dye, methylene blue (MB) as organic contaminant irradiated only under sunlight for a time period of 60 minutes. It was found that Cu doped NiO degrade MB much faster than pure NiO upon its exposure to sunlight. The experiment demonstrated that upon doping of copper, the photo-degradation efficiency of doped NiO was significantly enhanced. The prepared material proves to be a potential photocatalyst for degradation of dye polluted water.

Ullah et al. (2019) synthesized NiO NPs by using extraction from wastes of three different vegetables (cauliflower, potatoes and peas). The extracts of cauliflower and peas peels gave nanowhiskers while the extract of potato peels gave nanorods of NiO, as confirmed by scanning electron microscopy. The resulting NiO nanostructures were tested for their efficiencies as photocatalysts for Methylene blue degradation. The NiO nanostructures obtained by using cauliflower waste extract have degraded ~99% of MB dye in 120 min followed by those obtained with potato (~91.5) and peas (~67%) peel extracts.

Shanthakumari and Latha (2020) prepared using coprecipitation method NiO nps. XRD, FTIR spectroscopy, and FESEM, PL, and photocatalytic studies were characterized by the NiO nanomaterials. The XRD results showed that the crystalline structure of NiO NPs with a crystallite size of 34 nm was face-centered cubic (FCC). FESEM experiments have shown the formation and agglomeration of spherical-sized

nanocrystallites. The photocatalytic studies showed a degradation of methylene blue with efficiency of 65% for the NiO NPs.

Baygi et al. (2020) synthesized mixed-oxide TiO_2/NiO (50:50%) nanopowders using combustion based process in both acidic and alkaline solution. UV–visible spectroscopy results implied that single-oxide NiO, TiO_2, and TiO_2/NiO mixed-oxide NPs had narrow band gap values of 1.8, 2.6 and 2.5 eV, respectively. The narrow band gap energy of the combusted synthesized nanopowders improved theirphotocatalytic activity under the sunlight irradiation.Adsorption-desorption isotherm of the as-prepared powders showed the formation of porous powders with a specific surface area of 19, 22, and 192 m^2/g for NiO, TiO_2, and TiO_2/NiO particles, respectively. Results of the photocatalytic experiments under daylight emission using methylene blue (MB) as the dye molecule showed that degradation percentage of MB was more than 90% for all synthesized nanopowders.

Miri et al. (2020) synthesized, characterized, and applied the NiO NPs for degradation of methylene blue dye. The said NiO NPs were synthesized by using Zizyphus jujuba plant extract. The identification of prepared NiO NPs were done by using XRD, UV-Vis, Raman, FESEM, and EDX techniques. The temperature and time calcination was studied on size and morphology of synthesized NPs. By analysizing the photocatalytic assessment these NPs were capable of degrading the MB dye by 65.5%, in 180 min which can nominate them as a suitable option for being applied throughout the treatment of industrial wastewater. Akbari et al. (2020) investigated the effect of pH, light source, amount of photocatalyst, the initial concentration of dyes, light intensity, radiation time, the presence of mineral ions, and type of solvent. The prepared NiO NPs were used to analysed the degradation of methylene blue, methyl orange, and rhodamine B. The degradation percentage of methyl orange, rhodamine B, and methylene blue have been estimated to be around 84%, 79%, and 60%, respectively, after about 210 min. The degradation rate of methyl orange has been observed to be greater than methylene blue and Rhodamine B in the presence of UVA light irradiation. It was analysed that the photocatalyst process, the performance coefficient increases as the size of NiO particle becomes smaller; therefore, water treatment and removal of organic matter have become some of the essential applications of NiO NPs.

Motene et al. (2021) focused on the harmful effects of dyes present in the water. So they prepared flower like NiO NPs synthesized by using Sutherlendia frutescene plant extract. The results of SEM and XRD confirmed the formation of material through

morphological analysis and phase identification. These formed materials were used for the degradation of methylene blue and malachite green. NiO was a better photocatalyst towards Malachite green degradation than methylene blue, with a 98% degradation. Furthermore, the prepared NiO, was tested for its antibacterial efficacy against various model bacterial pollutants. It was found to be more active towards gram-positive bacteria (*E. faecalis*) compared to gram-negative.

3. Research Gap Identification

In present time, many researchers have studied synthesis of NiO NPs and after that doped the NiO by rare earth metal for various applications, but less work has been done trivalent metal doped NiO NPs. The present study will discuss the effect of doping, in mother element.

4. Objectives

The objectives of the study are given below

- To study the effect on structural, optical properties of pure and doped NiO NPs.
- To characterize the synthesize pure and doped NiO NPs by different techniques XRD, SEM, TEM, UV-Vis spectroscopy etc.
- To study the photocatalytic activity of the prepared pure and doped NiO NPs.

5. Proposed Methodology

5.1 Raw Materials

We have used materials to prepare the samples such as Nickel Chloride hexahydrate (98%, Alfa Aesar), NaOH (pellets) (98%,Alfa Aesar), distilled water, PVP (polyvinylpyrrolidone), Cerium(III) chloride heptahydrate (99%, Alfa Aesar), Gadolinium(III) chloride hexahydrate (99%, Alfa Aesar), methyl orange, methylene blue, rhodamine B, ethanol and distilled water.

5.2 Synthesis of pure NiO/Doped NiO nanoparticles

Pure NiO/Doped NiO NPs will be synthesis by co-precipitation method. For the synthesis of pure/doped NiO NPs, Nickel chloride hexahydrate and sodium hydroxide will be used as precursors. To stabilized the formed pure/Doped NiO NPs we will use polyvinylpyrrolidone (PVP) as capping agent. Dissolve nickel chloride hexahydrate in 100 ml of distilled water and stirrered for 30 minutes. After that the dopant of different concentration was added to the above reaction mixture.Add polyvinylpyrrolidone (PVP) which will dissolve in distilled water dropwise with continous stirrering. After that the sodium hydroxide solution will be

added dropwise untill the pH maintained at 12. Continue the strriring for 2 hours, filter the precipitates, gave the washing of these precipitates with distilled water and ethanol. At last we have to dried the formed NPs at 70 ^{o}C for 20 hours. The formed particles are calcined at 500 ^{o}C for 4 hours.

5.3 Characterization of synthesized pure NiO NPs and doped NiO NPs

The synthesized pure NiO and doped NiO NPs will be characterized to determine its various physical as well as chemical properties such as crystallite size, crystal structure, lattice parameters, band gap, surface morphology, particle size and dielectric properties. Various characterization techniques will be used for these parameters are X-Ray diffraction (XRD), UV-Visible spectroscopy (UV-Vis), Scanning electron microscope (SEM), Transmission electron microscope (TEM) and fourier transformed (FTIR) spectroscopy.

6. Photocatalytic activity

This study aims to assess the photocatalytic capabilities of NiO NPs doped trivalent metals. The evaluation will focus on the degradation of commercial dyes (rhodamine B, methylene blue, and methyl orange) through photocatalysis. The process involves monitoring the absorbance levels at specific time intervals using a UV-Vis spectrophotometer to track the degradation of the dyes.

7. Thesis Outline

The thesis will consists of the following chapters:

Chapter 1 (Introduction): This portion will contain brief introduction of NT, NPs, capping agent used along with characteristics of NiO NPs. It will also include the objectives of proposed work.

Chapter 2 (Literature Review): This chapter will contain literature with context of the synthesis, characterization and applications of pure NiO and doped NiO NPs with research gap identification.

Chapter 3 (Materials and methods): This chapter will comprise the detail of materials, chemical as well as coprecipitation synthesis, characterization techniques and applications of pure and doped NiO NPs.

Chapter 4 (Results and Discussion): This chapter will include the reports regarding physical and chemical properties of pure and doped NiO NPs along with analysis and comparison of the findings the work.

Chapter 5 (Summary and Conclusion): It will include the overall summary and conclusion of the entire study with regard to the work fulfill the required objectives which are cited.

Chapter 6 (References): All references are according to Harvard style.

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CERTIFICATE

(SYNOPSIS APPROVAL CERTIFICATE)

This is to certify that the Synopsis for Ph.D. Thesis titled, **"Study of Structural, Optical and Photocatalytic Exploration of Nickel Oxide Nanoparticles by the Incorporation of Trivalent Metal Ions",** submitted by **Ms. Shilpa Thakur** to the Career Point University, Hamirpur (H.P.), India in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY** in the Department of **Physics**, School of **Basic & Applied Sciences** has been approved by the Research Advisory Committee (RAC) after an Oral Examination of the student on dated 2 Jan, 2023.

Dr. Rajender Kumar, Asssociate Professor
Department of Physics
CPU, Hamirpur (H.P.)
(Supervisor)

Research Advisory Committee

Dr. Indu Sharma, Associate Professor
Department of Physics
CPU, Hamirpur (H.P.)
(Member)

Dr. Naveen Thakur, Professor
Department of Physics
CPU, Hamirpur (H.P.)
(Member)

Dr. Y.K Walia, Professor
Department of Chemistry
CPU, Hamirpur (H.P.)
(Member)

Dr. Naveen Thakur, Professor, CPU, Hamirpur (H.P.)
(Head)
Department of Physics

Dr. Kuldeep Kumar,
Associate Professor, CPU, Hamirpur (H.P.)
(Dean/ Associate Dean R & D)